IMPERIAL MYCOLOGICAL INSTITUTE
27 MAR. 1934

MASSACHUSETTS
AGRICULTURAL EXPERIMENT STATION

BULLETIN NO. 303 DECEMBER, 1933

Effect of Hydrocyanic Acid Gas on Cucumber Plants Previously Sprayed with Copper Fungicides

By E. F. Guba and E. B. Holland

The control of fungous diseases and insect pests of cucumbers in greenhouses frequently requires the use of copper fungicides and hydrocyanic acid gas. Complete destruction of greenhouse cucumber plantings has occurred in Massachusetts in some instances from such treatment. This study was undertaken to determine the nature and the range of this incompatibility and to formulate a safe procedure.

MASSACHUSETTS STATE COLLEGE
AMHERST, MASS.

EFFECT OF HYDROCYANIC ACID GAS ON CUCUMBER PLANTS PREVIOUSLY SPRAYED WITH COPPER FUNGICIDES

By E. F. Guba, Assistant Research Professor of Botany, and E. B. Holland, Research Professor of Chemistry

INTRODUCTION

The extensive greenhouse area devoted to the forcing of vegetables in Massachusetts has for many years necessitated study of control measures for insect pests and fungous diseases peculiar to these crops. Such studies have encouraged the use of fungicides and insecticides, and the intermingled application of these materials presents a problem of the utmost importance to the growers. One of these problems relates to the conflict existing between copper fungicides and hydrocyanic acid gas.

The understanding and solution of this problem has necessitated consideration of copper fungicides of different reaction, concentration, and composition and of different sources of hydrocyanic acid gas. The classification of the compatibility of copper fungicides with gas on cucumber plants and confirmatory knowledge obtained from chemical analyses of the spray residues would appear to contribute to our knowledge of the problem and suggest recommendations for a safe procedure.

HISTORICAL REVIEW

It has been noted by Guba (3, 4) that Bordeaux mixture and hydrocyanic acid gas are incompatible when gas follows spray in the greenhouse, and that when Bordeaux is used to control diseases tobacco fumigants should be substituted for the gas to avoid injury. Published information suggested that the gas (HCN) combined with copper to form cupric cyanide $Cu(CN)_2$, an unstable compound giving off cyanogen and leaving insoluble cuprous cyanide, Cu(CN).

Butler and Jenkins (1) have reported that as the ratio of lime to copper sulfate is increased in Bordeaux from 4-1-50 to 4-4-50 injury increases, and then decreases as the ratio is increased to 4-24-50. They claim that neutral Bordeaux, as represented by the formula 4-0.8-50, followed by gas is safe and that mixtures with high lime ratios, e.g. 4-16-50 and 4-24-50, are safe if the plants are kept dry after gas. According to these investigators, injury with certain ratios of lime to copper sulfate and none with others is correlated with the allegation that (a) insoluble cuprous cyanide is formed with a 4-0.8-50 mixture; (b) no cupric cyanide is formed with a 4-0.8-50 mixture but increasing amounts with mixtures up to 4-4-50, negligible amounts with 4-16-50 and none with 4-24-50; (c) the soluble double salt is formed in increasing amounts with 4-4-50 to 4-24-50 mixtures.

Quayle (13) was unable to confirm the safety of Bordeaux 4-0.8-50 with gas on lemon, but reported less injury than with Bordeaux 4-4-50, and that it was similarly graduated but more marked on increasing the interval between spray and gas. A spray of zinc sulfate and lime was safe, but it is not as effective as Bordeaux in controlling the brown rot disease caused by the fungus *Pythiacystis citrophthora* Sm. & Sm. It is, therefore, obvious, on the basis of our present state of knowledge of the problem, that further investigation is extremely desirable.

PRACTICAL CONSIDERATIONS INVOLVED

Copper fungicides are used to control some diseases of vegetable and ornamental crops under glass in Massachusetts. Bordeaux is frequently used to assist in the control of cucumber powdery and downy mildews, caused respectively by the fungi *Erysiphe cichoracearum* DC. and *Peronoplasmopara cubensis* (B. & C.) Clint., and no other commercial greenhouse crop in Massachusetts has been subject to greater destruction as the result of the incompatibility of Bordeaux with hydrocyanic acid gas. However, only 1-1-50 and 1-½-50 mixtures can be used since the higher concentrations cause hardening and stunting of growth. Some other minor uses for Bordeaux on greenhouse plants may be cited, but no diseases of greenhouse crops are known which require for their control such ratios of Bordeaux as 4-16-50 and 4-24-50. These mixtures are very difficult to apply, and the residue resulting on the sprayed leaf would obviously impair photosynthesis. A large excess of lime also reduces the concentration of the precipitated copper in the residue and acts as a deterrent to its fungicidal value.

According to Holland (7), the best ratio of milk of lime or hydrated lime to copper sulfate, as judged by suspension, is approximately a 4-2-50 mixture, and this might also be regarded as the lowest ratio practical from the standpoint of safety to the plant. Bordeaux 4-1-50 in practical preparation is not necessarily neutral, while 4-0.7-50 and 4-0.8-50 mixtures, even under laboratory preparation when the strength of the lime is previously determined, may show soluble copper. Practice makes little distinction with regard to the freshness of lime, neither has it adopted any simple qualitative tests to insure against a deficiency of lime. It is necessary, therefore, in practice to adhere rather closely to mixtures with a lime content in sufficient excess to eliminate water soluble copper. If it is true that hydrocyanic acid gas acting on neutral Bordeaux is safe, then the factor of practical preparation of such a mixture becomes important.

The allegation that 4-16-50 and 4-24-50 mixtures are safe with gas if the treated plants are kept dry does not take into consideration prevailing greenhouse conditions, notably high humidity, abundant transpiration, guttation, and high temperatures. There is no assurance of dry foliage even in the absence of wetting; neither are dry conditions under glass conducive to good plant growth.

EXPERIMENTAL METHODS

The cucumber plant was used to identify and measure the degree to which the copper residue is incompatible with gas, because it is extremely sensitive to injury from the combined copper and gas treatments. Potted plants were used. The sprays were applied with a quart atomizer and allowed to dry completely before exposure to gas. The plants were gassed in a tight greenhouse of a volume of 1500 cubic feet. Controls against gas and spray were included in each treatment.

Milk of lime, filtered lime water, and chemical hydrated lime were used with powdered copper sulfate in preparing lime Bordeaux. According to Holland, Dunbar and Gilligan (7) and Holland and Gilligan (10), chemical hydrated lime makes an excellent substitute for quicklime in the preparation of ordinary Bordeaux mixtures, and it is of such purity that it can be substituted pound for pound for quicklime. A chemical hydrated lime having a screen test of 98 per cent through 200 mesh and containing 73.72 per cent calcium oxide was used. When milk of lime was used, it was previously strained through a double thickness of cheesecloth. The method of mixing advocated by Holland, Dunbar and Gilligan (7) was adopted; namely, pouring dilute copper into concentrated lime. Accord-

ing to Butler[1], adding milk of lime to a 4-50 solution of copper sulfate until phenolphthalein paper turns red is more simple, and the mixture is as harmless as a strictly neutral wash. Both methods, however, have practical limitations.

In the experiments reported in this bulletin, different forms of lime and different kinds of base in different ratios with copper sulfate were used. Acid, neutral, and alkaline mixtures of Bordeaux 4-X-50 were prepared with filtered lime water and milk of lime. In many experiments the precipitates were washed on filter paper or by decantation and then brought to volume. Washing was intended to remove the excess of calcium hydroxide and some of the calcium sulfate, on the assumption that these materials might possibly be factors in the incompatibility of the spray with HCN gas.

Calcium cyanide, as Cyanogas, was used as the source of hydrocyanic acid gas in many of the experiments. The following tabulation shows the various ways in which it was used. The size of the fumigating chamber was 1500 cubic feet with a few exceptions which are noted.

Amount Used Grams	Period of Exposure Hours	Interval Between Copper Treatment and Fumigation Hours	Amount Used Grams	Period of Exposure Hours	Interval Between Copper Treatment and Fumigation Hours
4	12	32	7	10	8
4	12	36	7	12	8
5	12	40	8	10	10
5	12	96	10	10	8
6	10	10	10	10	10
6	10	32	10	10	36
6	10	34	25*	10	6
6	10	130	29†	12	8
6	11	8	87†	12	10
6	11	48	*Green house, 5, 000 cubic feet.		
6	12	10	†Greenhouse, 10,000 cubic feet.		

In other experiments, sodium cyanide was used at the rate of ¼ ounce to 1,000 cubic feet and in the generally accepted ratio of 1 ounce of sodium cyanide, 1½ ounces of concentrated sulfuric acid and 2 ounces of water by liquid measure. It is claimed that these proportions produce the maximum volume of gas and carry the reaction to completion. The plants were exposed to the gas as follows, beginning 1 to 2 hours after sundown.

Period of Exposure Hours	Interval Between Copper Treatment and Fumigation Hours	Period of Exposure Hours	Interval Between Copper Treatment and Fumigation Hours
1	8	3	8
2½	8	3	10
3	6	3	32

The greenhouse conditions to which the plants were exposed after gassing varied with the weather, but these were the usual commercial growing conditions prevailing under glass. The foliage of the treated plants was not at any time wetted with water. The results were recorded usually 3 to 6 days after exposure to gas.

Fungicides Employed

In the study of the effect of hydrocyanic acid gas on cucumber plants sprayed

[1]Letter from Dr O. Butler, dated April 22, 1932.

with copper fungicides, consideration was given to most of the diverse forms of copper sprays recommended by investigators or introduced by manufacturers, as classified by Holland and Gilligan (11). The effect of gas on plants sprayed with Bordeaux containing different ratios of lime to copper sulfate was especially investigated. Attention was also given to mixtures prepared with sodium carbonate and sodium hydroxide. Many proprietary Bordeaux substitutes were considered; namely, such brands as Corona, Bowker, Dow, Grasselli, Rex and Riches Piver. Such stainless copper sprays as ammoniacal copper carbonate, Fungtrogen and Hammond's Copper Solution were also tested. Other copper fungicides used were basic and normal copper acetates from the General Chemical Company, copper carbonates from the Corona Chemical Company, basic copper sulfate from Marsh Brothers, and factory-prepared basic copper sulfates of variable copper content prepared with calcium, magnesium, and sodium carbonates, and described by Holland et al. (6, 9).

Since it has been alleged that the reaction of the spray has a great bearing upon its compatibility with gas, the filtrates of the diluted sprays were carefully tested with litmus paper and a freshly prepared 10 per cent solution of potassium ferrocyanide. The chemical test is preferable to litmus for determining the presence of soluble copper and the reaction of the spray, but within narrow limits neither method, of course, indicates the amount of excess base.

RESULTS WITH CUCUMBER PLANTS

Lime with Copper Sulfate

In Table 1 are presented summarized data showing the effect on cucumber plants of a Bordeaux-hydrocyanic acid gas regime in which ratios of lime to copper sulfate were used ranging from 4-0.6-50 to 4-24-50.

When a 4-1-50 mixture was used, injury occurred after gas in each of the thirteen experiments, being severe or very severe in nine, moderate in one, and slight in three of the experiments (Figs. 1, 2). A litmus test of the filtrate applied in five experiments was neutral, and the copper test negative. When mixtures of 4-4-50, 4-8-50, 4-12-50, 4-16-50, and 4-24-50 preceded gas, severe injury occurred in each case (Fig. 1). In some instances injury increased as the ratio of lime to copper sulfate increased from neutral to 4-2-50 mixtures, while higher ratios showed a severe injurious effect which sometimes resulted in the death of the treated plants. The results of other experiments showed that the degree of injury with ratios of 4-1-50 to 4-8-50 was quite similar, or they showed only narrow distinctions (Fig. 1). Mixtures represented by the ratios 4-0.6-50 and 4-0.8-50, which yielded positive tests for copper, were of themselves injurious and the injury was greatly intensified by the action of gas. A 4-0.9-50 mixture prepared with milk of lime, giving a positive test for soluble copper, caused no injury of itself, but very severe injury when followed by gas. A similar mixture prepared with chemical hydrated lime and yielding no soluble copper caused injury with gas but no injury of itself. Thus, in six instances where soluble copper was detected in the diluted spray, the gas either caused or greatly intensified injury. When gas followed such weak Bordeaux mixtures as 1-½-50 (Fig. 2) and 1-1-50, injury resulted and this held as well when the sprayed plants were gassed 130 hours after the copper treatments as after 34 hours. No significant or consistent contrast in injury resulted from substituting milk of lime for chemical hydrated lime in the preparation of Bordeaux. A slight difference, however, in the purity of the lime products employed would be sufficient in the narrow ratios used to account for any slight difference in injury.

Plants sprayed with a 1-50 mixture of slaked pulverized "fat" lime treated with a 1 per cent solution of copper sulfate until neutral to litmus were killed by

TABLE 1. THE EFFECT ON CUCUMBERS PLANTS OF HCN GAS FOLLOWING TREATMENTS WITH LIME BORDEAUX MIXTURES, AND DETERMINATIONS OF SOLUBLE COPPER IN THE RESIDUE

Bordeaux Mixture	Reaction to Litmus	Reaction for Soluble Copper	Injury		Soluble Copper in Residue				HCN in Residue	
					On Leaves		On Glass		On Glass	
			Without HCN	With HCN	Without HCN	With HCN	Without HCN	With HCN	Without HCN	With HCN
4-0.6-50		+	+	+						
4-0.8-50		+	+	+			—	+	—	+
4-0.9-50		±[1]	—	+						
4-1-50	Neutral	—	±[2]	+	±[3]	+	—	+	—	+
4-2-50	Alkaline	—	—	+	—	+				
4-3-50		—	—	+	—	+				
4-4-50		—	—	+	—	+	—	+	—	+
4-4-50 filtered and washed			—	+						
4-4-50 filtrate			—	—						
4-6-50			—	+	—	+				
4-8-50			—	+	—	+	—	+	—	+
4-12-50			—	+	—	+				
4-16-50			—	+			—	+	—	+
4-24-50			—	+			—	+	—	+
1-½-50	Alkaline	—	—	+						
1-1-50			—	+						
1-4-50			—	+						
2-4-50			—	+						
3-4-50			—	+						
4-X-50 (Milk of Lime)	Acid	+	±[4]	+		+				
	Neutral	—	—	+			±[5]	+		
	Alkaline		—	+		+				
4-X-50 (Milk of Lime) washed	Acid	+	—	+						
	Neutral	—	—	+						
	Alkaline		—	+						
4-X-50 (Milk of Lime) filtrate	Neutral	—	—	—						
	Alkaline	—	—	—						
4-X-50 (Filtered Lime Water)	Acid	+	+	+		+				
	Neutral	—	—	+		+				
	Alkaline		—	+		+				
4-X-50 (Filtered Lime Water) Washed	Acid	+	+	+		+				
	Neutral	—	—	+		+				
	Alkaline		—	+		+				
4-X-80 (Filtered Lime Water)	Neutral	—	—	+			—	+		
4-X-100 (Filtered Lime Water)	Neutral	—	—	+						

[1]Two samples prepared with chemical hydrated lime gave a negative reaction for soluble copper; two samples prepared with milk of lime from fresh calcium oxide gave a positive reation.
[2]There was no injury in twelve tests; in one test there was slight injury
[3]No soluble copper in one test; slight trace in two.
[4]No injury in two cases; injury in two cases
[5]Soluble copper in one test; none present in three.

exposure to HCN. When the order of mixing was reversed and a milk of lime suspension was employed, the effect after HCN was the same. A 0.5 per cent solution of copper sulfate neutralized with filtered lime water caused slight injury with HCN. A 1 per cent solution of copper sulfate was neutralized with filtered lime water and allowed to settle. The top, clear liquor was decanted and to the sediment was added fresh water to make 500 cc. When cucumber plants were sprayed with this mixture and then gassed, the injury was moderate to severe. Plants were killed when gas followed the use of a 4-50 solution of copper sulfate neutralized with milk of lime, and were severely injured when gas followed Bordeaux 4-X-50 neutralized with filtered lime water prepared from fresh stone lime.

Acid, neutral, and alkaline 4-X-50 mixtures prepared with milk of lime and filtered lime water, and either used as such or first washed and dehydrated, were compared to determine the influence of the form of lime and the reaction of the spray on the compatibility of the residue with the gas (Tables 1, 5). When acid Bordeaux 4-X-50 prepared with milk of lime was employed, slight injury resulted in two instances and none in two; but on exposure of the sprayed plants to gas, injury resulted in every instance, and it was intensified in the two cases in which the spray itself was injurious. Neutral mixtures of 4-X-50 prepared with milk of lime were safe of themselves, but in every instance they were injurious with gas. Similar mixtures containing sufficient excess lime to give an alkaline test to litmus gave like results. When these mixtures were washed, none caused injury of themselves, even the acid mixtures, yet all of them were injurious when the sprayed plants were exposed to gas. When Bordeaux 4-X-50 was prepared with filtered lime water, only the acid mixtures caused injury of themselves. Injury resulted in every instance where gas acted on neutral or alkaline mixtures, and it was intensified by the action of gas on acid mixtures. Washing the mixtures did not effect any change in these results. Washing and dehydrating a neutral 4-X-50 mixture prepared with milk of lime or filtered lime water (Table 5) then bringing again to volume with water did not make it safe to use, but prolonging the interval between spraying and gassing appeared to remove or lessen the danger of injury. The filtrates of neutral or alkaline Bordeaux 4-X-50 mixtures were compatible with gas, indicating that the incompatible principle is not present in the filtrate and that it is neither calcium hydroxide nor calcium sulfate. (Fig. 3.)

On the basis of this experimentation, it may be concluded that slightly acid or neutral Bordeaux mixtures of lime and copper sulfate which are safe of themselves are positively incompatible with hydrocyanic acid gas; that mixtures with increasing amounts of lime are extremely fatal to cucumbers under commercial conditions of culture; that Bordeaux made with milk of lime or chemical hydrated lime results in more injury when followed by gas than Bordeaux made with lime water, although none are safe. The presence of moisture on the foliage such as would occur from watering is not a necessary factor. Irrespective of the ratio of lime to copper sulfate, injury will occur and the most severe damage may be expected with mixtures containing an excess of lime.

Sodium Carbonate with Copper Sulfate

Burgundy precipitates of different ratios of sodium carbonate to copper sulfate were prepared by adding a cool, dilute solution of copper sulfate to a similar solution of sodium carbonate, then bringing up to volume (Table 2). Burgundy 4-4-50, a strongly alkaline precipitate, was employed three times, causing some injury of itself in two experiments but none in the third. In all three experiments exposure of the sprayed plants to hydrocyanic acid gas was fatal to the plants. Precipitates of 4-2-50 and 4-3-50 ratios, also alkaline to litmus, caused no injury

of themselves; but with gas injury resulted in all instances. An acid 4-X-50 mixture in one experiment was safe of itself but caused severe injury with gas; in another experiment injury was severe both from the spray itself and with gas. When a neutral mixture was employed, slight injury resulted from the spray in one experiment and none in another; but gas in both instances either caused or increased the degree of injury. In one instance a 4-X-50 mixture, containing sufficient excess of sodium carbonate to give an alkaline test with litmus, caused severe burning of itself, and the plants were killed after exposure to gas.

The results with Burgundy precipitates show that the degree of injury following gas is not correlated with any particular reaction of the spray used. The unstable character of this precipitate even in the absence of gas is a sufficient hazard to discourage its use on greenhouse cucumbers.

TABLE 2. THE EFFECT ON CUCUMBER PLANTS OF HCN GAS FOLLOWING TREATMENTS WITH SAL SODA AND CAUSTIC SODA BORDEAUX MIXTURES, AND DETERMINATIONS OF SOLUBLE COPPER IN THE RESIDUE.

Fungicide	Reaction to Litmus	Reaction for Soluble Copper	Injury		Soluble Copper in Residue on Leaves	
			Without HCN	With HCN	Without HCN	With HCN
Burgundy Mixture 4-X-50	Acid	+	±[1]	+		
	Neutral		±[2]	+	+	+
	Alkaline		+	+		
Burgundy Mixture 4-2-50	Alkaline	—	—	+	—	+
Burgundy Mixture 4-3-50	Alkaline	—	—	+		
Burgundy Mixture 4-4-50	Alkaline	—	±[3]	+		
Caustic Soda Bordeaux 4-X-50	Acid	+	±[4]	+		+
	Neutral	—	±[5]	+	±[6]	+
	Alkaline		—	+		
Caustic Soda Bordeaux 4-2-50	Alkaline	—	—	+		

[1] Injury in one case; no injury in two.
[2] Slight injury in one case; no injury in one.
[3] Injury or slight injury in two cases; no injury in one.
[4] Injury in two cases; no injury in one.
[5] Injury in one case; no injury in four.
[6] Trace of soluble copper in one case; none in one case.

Sodium Hydroxide with Copper Sulfate

In Table 2 is shown the effect of hydrocyanic acid gas on plants sprayed with sodium hydroxide and copper sulfate in different ratios. When acid 4-X-50 mixtures of caustic soda and copper sulfate were employed, injury resulted from the spray itself in two of three instances. In the third case injury resulted only after exposure to gas. A neutral mixture was used in five experiments, the spray itself causing injury in only one case, but injury resulting from the use of gas in each case. Where alkaline mixtures of 4-X-50 and 4-2-50 ratios were used, injury followed exposure of the sprayed plants to gas, but no injury occurred without gas.

It may be stated that mixtures prepared from sodium hydroxide and copper sulfate, irrespective of the reaction of the spray, are not safe with HCN on cucumbers, and it is concluded that the ratio of sodium hydroxide to copper sulfate does not materially influence the degree of injury.

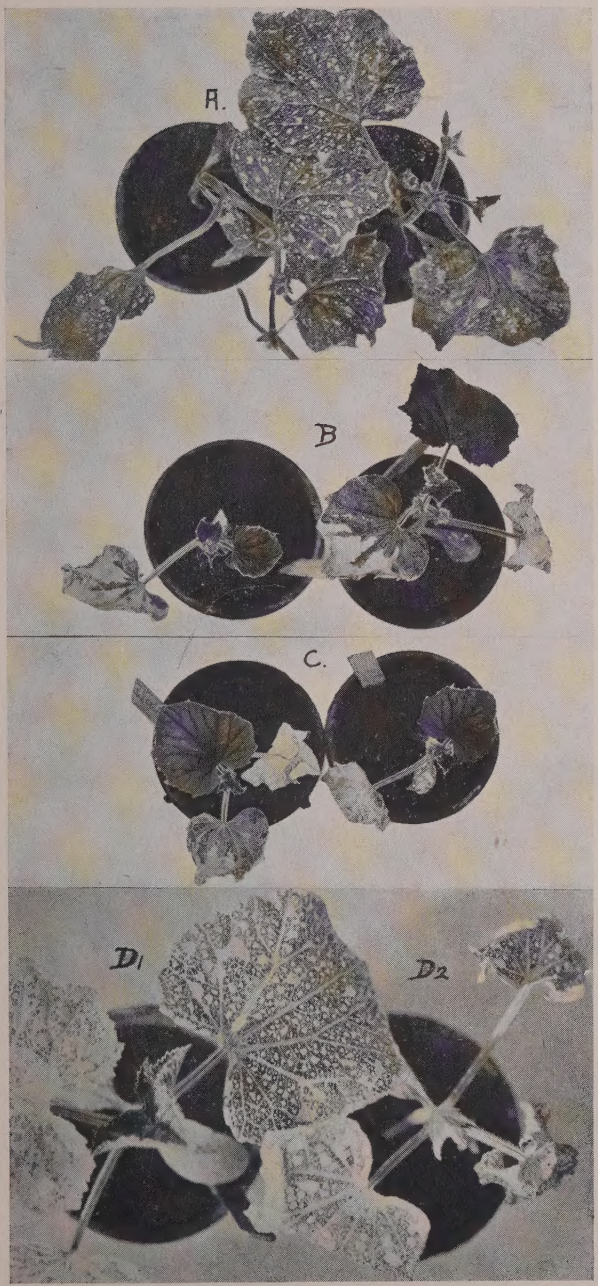

Figure 1.—Cucumber Plants Sprayed with Bordeaux and Gassed with HCN.
A, Bordeaux 4-1-50; B, 4-4-50; C, 4-8-50; D1, 4-24-50 without HCN; D2, 4-24-50 with HCN. Note that injury has occurred with all mixtures when followed by gas.

Figure 2.—Cucumber Plants Sprayed with Bordeaux and Gassed with HCN.
A, Bordeaux 4-1-50; B, 1-½-50; C, Control, gassed only. Note that neither Bordeaux 4-1-50 nor Bordeaux 1-½-50, which contains an excess of lime but only one-fourth as much copper sulfate, is safe with gas.

Figure 3.—Cucumber Plants Sprayed with Bordeaux and Gassed with HCN.
A, sprayed with filtrate of neutral Bordeaux 4-X-50; B, Control gassed only; C, sprayed with washed residue of neutral Bordeaux 4-X-50; D, complete spray of neutral Bordeaux 4-X-50. The incompatible component of the spray is in the washed residue and not in the clear filtrate.

Figure 4.—Cucumber Plants Sprayed with Normal and Basic Copper Acetates and Gassed with HCN.

A, a 0.5 per cent solution of basic copper acetate (34.4 per cent Cu); B, a 0.34 per cent solution of basic copper acetate (48 per cent Cu); C, a 0.54 per cent solution of normal copper acetate (31.8 per cent Cu). Right, gassed with HCN; left, not gassed.

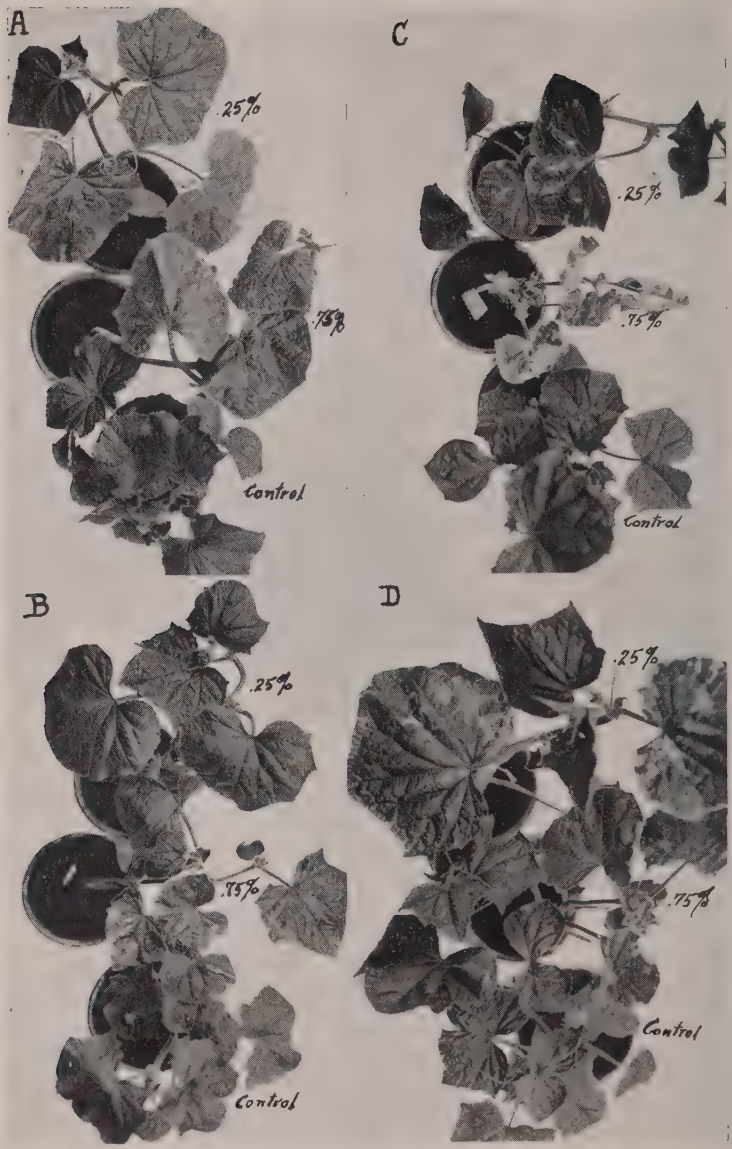

Figure 5.—Cucumber Plants Sprayed with Normal and Basic Copper Acetates of 0.25 and 0.75 Per Cent Strengths and Gassed with HCN.

A, basic copper acetate (34.4 per cent Cu) without gas; C, with gas; B, normal copper acetate (31.8 per cent Cu) without gas; D, with gas. All controls gassed only. Injury occurs after the action of gas, irrespective of the presence of alkali in the spray.

Dry Bordeaux Substitutes

In Tables 3 and 5 are presented the results of the use of HCN gas on cucumber plants previously sprayed with proprietary Bordeaux powders. These sprays were prepared to contain the same amount of copper that is present in 4 pounds of crystalline copper sulfate in 50 gallons of Bordeaux. The Dow and Rex brands of Bordeaux powders are slightly alkaline. The Corona, Riches Piver, Grasselli, and Bowker brands are more strongly alkaline to litmus. In every case severe injury occurred after the sprayed plants were gassed. This fact, however, is not to be construed as casting any reflection upon these materials as fungicides when used in the absence of gas. The reaction of these sprays within the limits shown by a litmus paper test was not a factor in influencing the degree of injury.

TABLE 3. THE EFFECT ON CUCUMBER PLANTS OF HCN GAS FOLLOWING TREATMENTS WITH CERTAIN PROPRIETARY COPPER FUNGICIDES, AND DETERMINATIONS OF SOLUBLE COPPER IN THE RESIDUE.

Fungicide	Active Cu Content Per Cent	Reaction to Litmus	Reaction for Soluble Copper	Injury		Soluble Copper in Residue			
						On Leaves		On Glass	
				Without HCN	With HCN	Without HCN	With HCN	Without HCN	With HCN
Basic Copper Sulfate	26.31	Neutral	—	—	—	—	±[1]	—	±[2]
Basic Copper Sulfate	52.95	Neutral	—	—	—				
Basic Copper Sulfate	53.31	Neutral	—	—	—				
Basic Copper Sulfate plus 0.1% Chem. Hyd. Lime	26.31	Alkaline	—	—	+	—	+		
Basic Copper Sulfate plus 0.2% Chem. Hyd. Lime	26.31	Alkaline	—	—	+				
Basic Copper Sulfate plus 0.5% Chem. Hyd. Lime	26.31	Alkaline	—	—	+	—	+	-	
Basic Copper Sulfate plus 1.0% Chem. Hyd. Lime	26.31	Alkaline	—	—	+	—	+		
Chem. Hyd. Lime 0.2%, 0.5%, 1.0%		Alkaline	—	—	—				
Bordow (Dow)	12.75	Alkaline[3]	—	—	+	+[4]	+	—	+
Bordeaux Mix. Pow. (Grasselli)	13.	Alkaline	—	—	+				
Bordo Mix. (Rex)	16.	Alkaline[3]	—	—	+				
Corona Copper Carbonate	50.	Neutral	—	—	—				
Corona Copper Carbonate	18.	Neutral	—	—	±[5]	+[4]	±[6]	—	±[7]
Bordeaux (Riches Piver)	12.75	Alkaline	—	—	+				
Dry Bord. Mix. (Corona)	13.	Alkaline	—	—	+				
Dry Pow. Bord. (Bowker)	13.	Alkaline	—	—	+				

[1] Trace of soluble copper in three cases; none in one.
[2] Trace of soluble copper in five cases; none in two.
[3] Only slightly alkaline.
[4] Slight trace of soluble copper in one case.
[5] Trace of injury in one case; none in three.
[6] Soluble copper in two cases; none in one
[7] Trace of soluble copper in one case; none in one.

Factory-made basic copper sulfates, the preparation of which is fully reported by Holland et al. (6, 9), caused no injury of themselves or with gas. These sprays are neutral to litmus and were prepared with calcium carbonate, magneisum carbonate, or sodium carbonate. In preparation the heated precipitates are washed practically free of soluble by-products, i.e., magnesium and sodium sulfates, then dried and air separated. The addition of chemical hydrated lime, in 0.1, 0.2, 0.5, and 1.0 per cent strengths, to diluted 26 per cent basic copper sulfate caused injury with gas which was most severe, generally considered, with the highest amounts of lime added. Corona copper carbonate powders, containing 18 per cent and 50 per cent copper, and basic copper sulfate (Marsh Bros.), containing 53 per cent copper, are neutral to litmus and were also safe with gas. The Corona 18 per cent product is similar in preparation to the 26 per cent basic copper sulfate, and the Corona 50 per cent product to the 53 per cent basic copper sulfate. Greater stability is obtained in the manufacture of basic copper sulfates and carbonates by heating the precipitates, and this appears to explain their safety with HCN. The Marsh Bros. product is produced by the action of ionized copper sulfate or of sulfuric acid on metallic copper and contains no by-products.

Stainless Copper Sprays

This group includes copper acetate (Table 4), Hammond's Copper Solution, Fungtrogen, and copper sulfate.

Table 4. The Effect on Cucumber Plants of HCN Gas Following Treatments with Certain Stainless Copper Sprays.

Fungicide	Active Cu Content Per Cent	Concentration	Reaction to Litmus	Reaction for Soluble Copper	Injury	
					Without HCN	With HCN
Hammond's Copper Sol.	3.04	a	Alkaline	—	—	±
Fungtrogen	0.47	b	Alkaline	—	—	—
Ammoniacal Copper Carbonate		c	Alkaline	—	—	—
Basic Copper Acetate	34.4	d	Acid	+	±	+
Normal Copper Acetate	31.8	e	Acid	+	±	+
Copper Sulfate .01% Sol.			Neutral	Trace	—	—
Copper Sulfate .02% Sol.			Neutral	Trace	—	—
Copper Sulfate .03% Sol.			Neutral	Trace	—	—
Copper Sulfate .05% Sol.			Neutral	Trace	—	—
Copper Sulfate .07% Sol.			Acid	Trace	—	—

a—1-80 in 4 instances; 1-40 (double the manufacturer's recommendation) in one. Slight injury occurred in two cases at the 1-80 concentration; no injury in the other cases.
b—1-60 in 3 instances; 1-30 (double the manufacturer's recommendation) in one.
c—NH_4OH 0.8% with $CuCO_3$ 0.24, 0.16, and 0.08 % by weight.
d—0.25, 0.50, and 0.75 % by weight. Injury without HCN in 2 cases; no injury in 4 cases.
e—0.25, 0.50, 0.65, 0.75, and 0.80 % by weight. Injury without HCN in 2 cases; no injury in 3 cases.

Basic copper acetate, containing 34.4 per cent copper, and normal copper acetate, containing 31.8 per cent copper, were used. Both forms gave positive tests for soluble copper and acid reactions to litmus. Basic copper acetate was used at strengths of 0.25, 0.50, and 0.75 per cent by weight, and normal copper acetate at strengths of 0.25, 0.50, 0.65, 0.75, and 0.80 per cent. Since both products contain over 30 per cent of copper, a concentration of 0.25 per cent would contain over 0.07 per cent copper, which would seem fairly reasonable, although references state that they have been used at concentrations ranging from less than 0.1 to 1

TABLE 5. THE EFFECT ON CUCUMBER PLANTS OF HCN GAS FOLLOWING TREATMENTS WITH COPPER FUNGICIDES

	Fumigation Treatment			
	I	II	III	IV
Cyanogas Used.....grams	4½	4½	4½	5
Period of Exposure.....hours	10	12	10	10
Interval Between Copper Treatment and Fumigation.....hours	9	32	57	105

Copper Treatment	Type of Injury After Exposure to HCN Gas			
	I	II	III	IV
No treatment	Slight	None	None	None
Basic Copper Sulfate 26%	Slight yellowing of leaf margins	None	None	None
Corona Copper Carbonate 18%	None	None	None	None
Basic Copper Sulfate 53% (Marsh)	Slight	None	None	None
Neutral Bordeaux 4-X-50 (Milk of Lime)	Severe to very severe	Moderate to severe	Slight to moderate	Slight
Neutral Bordeaux 4-X-50 (Milk of Lime) washed	Very severe	Moderate	Moderate	Slight
Neutral Bordeaux 4-X-50 (Milk of Lime) washed, dried and brought to volume	Moderate to severe	Slight trace	None	None
Neutral Bordeaux 4-X-50 (Filtered Lime Water)	Very severe	Severe or very severe	None	None
Neutral Bordeaux 4-X-50 (Filtered Lime Water) washed	Very severe	Severe	Slight	Very slight
Neutral Bordeaux 4-X-50 (Filtered Lime Water) washed, dried and brought to volume	Trace; chronic yellow along margins	Slight; chronic yellow	Trace to slight	None
Bordeaux 4-4-50 Chem. Hyd. Lime	Killed	Very severe	Moderate	Moderate to severe

per cent with no well-defined practice. Basic copper acetate was injurious in two out of six experiments, and normal copper acetate in two out of five (Fig. 4). This may have been due to some difference in the amount of spray applied or to variations in atmospheric conditions in the greenhouse. Injury followed the exposure of the sprayed uninjured plants to gas; and in those instances where injury resulted from spraying, it was intensified by the action of gas. The soluble copper salt formed by the action of gas was much more toxic than copper acetate itself. A 0.25 per cent dilution was less injurious than higher concentrations, this also holding true with gas (Fig. 5).

Copper sulfate in 0.01, 0.02, 0.03, and 0.05 per cent solutions was neutral to litmus but gave faint positive chemical tests for soluble copper. A 0.07 per cent solution was acid to litmus. In none of the experiments were cucumber plants injured by copper sulfate sprays used alone in these concentrations or by the exposure of the sprayed plants to gas. It is evident, therefore, that cucumber plants will tolerate a small amount of water soluble copper without manifesting injury.

Hammond's Copper Solution, an ammoniacal copper concentrate guaranteed to contain 3.05 per cent active copper, was not injurious to cucumbers of itself

at dilutions of 1-80 and 1-40, but slight injury followed the use of gas in two cases out of five. Lack of injury beyond a slight degree in two instances is attributed to the relatively small concentration of copper present as compared to a 4-50 strength of copper sulfate in Bordeaux. Stronger solutions were unsafe for cucumber plants.

Fungtrogen, containing 0.47 per cent active copper and 0.47 per cent nickel and alkaline to litmus, caused no injury of itself or with HCN at dilutions of 1-30 and 1-60. The low concentrations, like the low concentrations of copper sulfate, undoubtedly account for its safe use with gas.

Laboratory-prepared ammoniacal copper carbonate was not toxic to cucumber plants of itself or with HCN in any strength of copper carbonate ranging from 0.08 to 0.24 per cent in 0.8 per cent ammonium hydroxide solution.

It is evident from these results that more than mere traces of soluble copper must result from the action of gas on copper residues in order to cause injury, and that the copper content of the fungicide is a contributing factor in the reaction.

Lime

When sprays of chemical hydrated lime of 0.2, 0.5 and 1 per cent strengths were used, no injury occurred from the sprays either alone or with gas.

EFFECT OF HYDROCYANIC ACID GAS ON COPPER SPRAY RESIDUES

On Cucumber Leaves

An explanation for injury to sprayed plants from the action of HCN gas on the spray residue was sought in qualitative tests of the residue after fumigation. The dry spray residues from the surface of 10 grams of leaves were carefully collected with distilled water, the washings filtered, and the filtrate tested for soluble copper with potassium ferrocyanide.

The residues of Bordeaux on cucumber leaves acted upon by HCN gas yielded positive tests for water soluble copper (Table 1). In three experiments a test was made of the residue of Bordeaux 4-1-50, a neutral mixture, on cucumber leaves. In one of three instances in which the plants were not exposed to gas, no soluble copper was found, and in the other two only a slight trace; while the action of the gas resulted in the presence of much soluble copper and in injury in all three instances. Bordeaux mixtures containing higher amounts of lime, e.g., 4-2-50, 4-3-50, 4-4-50, 4-6-50, 4-8-50, and 4-12-50, when exposed to gas yielded soluble copper, and cucumber foliage was injured in every instance. The degree of injury and the amount of soluble copper in the residue increased as the ratio of lime to copper sulfate was increased. The residues of neutral and alkaline Bordeaux 4-X-50 mixtures, prepared with milk of lime or filtered lime water and either washed or not, consistently yielded soluble copper after the action of gas, and its presence was associated with foliage injury. Similarly the residue of a neutral 4-X-50 Burgundy mixture yielded but a trace of soluble copper, while the action of gas resulted in much of it; and the residue of neutral caustic soda Bordeaux 4-X-50 showed only a trace of soluble copper in one instance and none in the other, while after the action of gas strong tests were obtained in both cases (Table 2).

The results with basic copper sulfates (Table 3) are particularly interesting because the lack of injury from these materials was definitely correlated with the compatibility of their residues on leaves with gas. In three of four tests only a trace of copper was detected, and in the fourth test none. However, when chemical hydrated lime was added to basic copper sulfate and the sprayed plants exposed to gas, good tests for soluble copper were obtained in each of seven experiments,

indicating the influence of excess base as a contributing factor in the production of soluble copper. Injury occurred only when lime was added to the basic copper sulfates, and the amount of soluble copper found increased in proportion to the amount of lime added. Corona 18 per cent copper carbonate with gas gave positive tests for copper in leaf residues in two instances and none in the third, but no foliage injury resulted in either of the cases where soluble copper was found.

There is sufficient evidence here to affirm that the fact that a copper spray is neutral or approximately neutral in laboratory preparation is no insurance against the production of soluble copper on the leaf and consequent injury. Factory-prepared basic copper sulfates and carbonates are safe, apparently because of their greater stability.

On Glass

In the previous section it was shown that the copper residue on the sprayed leaf gives rise to a soluble copper salt in the presence of HCN. This may indicate the participation of the plant itself in the reaction, for according to Crandall (2), Holland, Dunbar and Gilligan (8), and Pickering (12), complex soluble cupric compounds of copper may be produced from copper fungicides by alkali and exudation products of the plant, or by osmosis of the cell contents such as sugars, hydroxy-organic acids, and biuret compounds. It is also possible that certain inconsistencies in the tests for soluble copper in the residues on leaves may be correlated with leaf action, although other factors such as dosage, period of exposure, atmospheric conditions, and any narrow differences arising in the compounding of the sprays are also to be considered as contributing factors. As a matter of investigation, panes of glass 16 by 30 inches were sprayed with Bordeaux mixtures of different ratios of lime, ranging from neutral to 4-24-50 mixtures, and allowed to air dry. Exposure to gas was over night. Controls against the action of gas were included in each experiment. The dry residues were removed and examined for color, soluble copper, and HCN.

A given weight of dry residue, generally 1/10 gram, was macerated in water and tested for soluble copper. Another 1/10 gram of residue was macerated with water and tested for hydrocyanic acid.

Dry residues of Bordeaux, increasing in ratios of lime from neutral to 4-24-50 mixtures exhibited increasing intensities of blue color ranging from pale nile or lumiere blue to pale king's blue, according to the color chart of Ridgway (14). Parallel residues of the same mixtures exposed to gas exhibited colors of rejane and deep lichen green (4-0.8-50 to 4-4-50); glaucous, pale glaucous green, corydalis green, and yellowish glaucous (4-4-50 to 4-16-50); and pale dull glaucous blue (4-24-50). Butler and Jenkins (1) obtained brown precipitates on passing hydrocyanic acid gas into toxic Bordeaux mixtures and white precipitates with non-toxic mixtures such as 1:0.2 and 1:6. In the experiments of the writers, brown or white residues were never obtained when gas acted on Bordeaux on glass, irrespective of the ratio of the base to copper sulfate. Therefore, if brown precipitates suggest cupric cyanide and white precipitates cuprous cyanide, neither of these compounds was present. Bordeaux mixture increasing in ratios of lime from 4-0.8-50 to 4-24-50 showed soluble copper and HCN in residues on glass after exposure to gas in each of sixteen tests. The neutral mixtures prepared with milk of lime and chemical hydrated lime were no exception (Table 1). Parallel residues not exposed to gas were in every instance free of soluble copper and HCN. The change in color of the residue on exposure to gas, therefore, is correlated with the production of soluble copper, although the color could not be considered a safe guide as to the amount present. Butler and Jenkins contend that Bordeaux 1:0.2 and 1:6 ratios do not give off detectable amounts of cyanogen,

while 1:1 and 1:2 ratios give off the largest amounts and most rapidly. In the present experiments, all of the gas-treated residues contained hydrocyanic acid gas and this increased with the amount of lime in the Bordeaux.

The results indicated that an increase in the ratio of lime from neutral to 4-8-50 and 4-12-50 resulted in a corresponding increase in the amount of soluble copper and HCN. Further increase in the ratio of lime up to 4-24-50 resulted in a gradual decrease in the amount of soluble copper, but did not render the spray and gas regime safer to cucumber plants. Since qualitative analyses of the residues were based on an equal weight, namely 1/10 gram, the copper content obviously should vary with the concentration of lime. Assuming that 4 pounds of crystalline copper sulfate (25.46 per cent Cu) are employed in preparing Bordeaux, then the amount of copper in the residue would vary with the proportion of lime. The applications, although approximately of the same value of Bordeaux in each case, are therefore not directly comparable as regards the relative amounts of soluble copper found. This fact accounts for an eventual decrease in the amounts of soluble copper as the lime content is increased above ratios of 4-8-50 and 4-10-50, based on an equal weight of the dry samples analyzed.

Dow Bordow, which is an alkaline proprietary copper powder, yielded considerable soluble copper on exposure to gas, but none by itself in two parallel tests (Table 3). Being alkaline, these powders behave like Bordeaux mixtures containing an excess of lime.

The residue of factory-made basic copper sulfate (26.31 per cent Cu) on glass when exposed to HCN never yielded sufficient soluble copper to cause injury. When residues were exposed to gas, a trace of soluble copper was found in five instances and none in two. No soluble copper was found in any of the residues not exposed to gas. The results with Corona copper carbonate (18 per cent Cu) were similar.

Three tests of the residues of neutral Bordeaux 4-X-50 prepared with milk of lime showed no soluble copper; but after exposure to gas, soluble copper was present in all three, although in one case there was only a trace (Table 1). In another comparative test of this mixture, soluble copper was found in both residues, but that acted upon by HCN contained the greater amount. When residues of neutral 4-X-50 mixtures prepared with filtered lime water were compared, a trace of copper was found only in residues exposed to gas, and in each instance the Bordeaux and gas regime caused injury to cucumber foliage.

The analysis of spray residues on glass offered more consistent results than on leaves, indicating some influence of the respiratory or transpiratory products or of exudation of the leaf itself.

The action of HCN gas on factory-prepared neutral basic copper sulfates and carbonates did not produce sufficient soluble copper to cause injury to cucumber plants. Gas reacted with neutral laboratory-prepared Bordeaux, and the amount of soluble copper formed appeared to be greater when dispersed lime was used in preparation, e.g., milk of lime or chemical hydrated lime, than when a solution of lime such as filtered lime water was used, but the nature of the base did not remove the hazard of injury. Laboratory preparation in the cold produces less stable copper sulfates than heating which is the practice in the manufacture of commercial sulfates and carbonates; while washing, dehydration, and air separation of the commercial sulfates and carbonates are considered less important factors contributing to their safety with HCN gas. The results show beyond doubt that homemade neutral Bordeaux 4-X-50, even if its preparation were practical, is not safe with gas.

It is logical to assume that a soluble double salt is formed in all cases when hydrocyanic acid gas acts on Bordeaux mixture and that the amount varies with the amount of free base, the concentration of the gas, the period of exposure to

gas, the conditions favoring absorption of the gas, and the greenhouse temperatures after gas. Water soluble copper would seem to preclude cuprous and cupric cyanides also, since both are insoluble in water, according to Williams (15, p. 48-49) and Hodgman and Lange (5, p. 102, 103). Cuprous cyanide readily dissolves in solutions of alkaline cyanides with which it forms a number of crystalline double salts. The calcium salt $CaCu_2(CN)_4 5H_2O$, according to Williams (15) is very soluble in water. The injurious compound formed when gas acts on Bordeaux is presumably calcium cuprocyanide or some similar product. An equation showing the procedure in the reaction, or a more definite opinion regarding the formula of the toxic substance would be dangerous without more confirmatory laboratory work, and is not needed from a practical point of view.

CONCLUSION

The presence of free lime or soda in the copper spray increases the degree of injury; but injury may occur without it as is demonstrated by the behavior of acid Bordeaux mixtures prepared with lime or soda, the acid basic and normal copper acetates, and neutral Bordeaux 4-X-50 mixtures prepared with milk of lime or filtered lime water. The danger of injury from the use of insufficient lime would be as great as the danger from a slight excess. Therefore, if fungous diseases are of sufficient importance in the greenhouse to warrant the use of copper fungicides, fumigation with hydrocyanic acid gas should precede the application of copper; or only commercial basic copper carbonates, basic copper sulfates, or non-staining ammoniacal copper sprays should be used.

SUMMARY

Cucumber plants were not injured when sprayed with Corona copper carbonate (18 or 50 per cent Cu) or commercial basic copper sulfates (26.31, 52.95, or 53.31 per cent Cu) followed by hydrocyanic acid gas. These diluted sprays are neutral to litmus. Laboratory-prepared neutral Bordeaux mixtures with gas were injurious.

When cucumber plants were sprayed with basic copper sulfate to which chemical hydrated lime had been added, injury followed the use of gas and increased proportionately with the alkali present.

When cucumber plants were sprayed with acid copper fungicides, i.e., normal and basic copper acetates, acid Bordeaux prepared with calcium hydroxide, sodium carbonate, or sodium hydroxide, injury resulted from or was intensified by an application of gas.

Copper sulfate solutions containing 0.01, 0.02, 0.03, 0.05, or 0.07 per cent copper sulfate were not injurious to cucumber plants when used alone or followed by gas.

Cucumber plants were injured when gas followed spraying with copper fungicides containing calcium hydroxide, sodium hydroxide, or sodium carbonate, even when the alkali component was reduced to yield mixtures neutral to litmus.

Injury occurred whether hydrocyanic acid gas was evolved from calcium cyanide (Cyanogas) or from sodium cyanide, and whether chemical hydrated lime, milk of lime, or filtered lime water was used in the preparation of Bordeaux.

The spray residue from injured leaves yielded water soluble copper; and the amount of soluble copper and the degree of injury in general tended to increase in proportion to the amount of alkali present in the fungicide within the limits of ordinary ratios of base to copper sulfate.

Residues of Bordeaux on glass, acted upon by gas, yielded both soluble copper and hydrocyanic acid gas. These occurred in a fairly constant ratio and increased

in proportion to the amount of alkali present. A large excess of alkali reduced the concentration of precipitated copper in the spray and consequently the amount of soluble copper in the gassed residues.

The toxic salt is presumably calcium cuprocyanide $CaCu_2(CN)_4 5H_2O$ or a similar soluble copper salt of cyanide.

LITERATURE CITED

1. Butler, L., and Jenkins, R. R. Effect on plants of cyanide fumigation following spraying with Bordeaux mixture. Phytopath. 20:419-429. 1930.
2. Crandall, C. S. Bordeaux mixture. Ill. Agr. Expt. Sta. Bul. 135. 1909.
3. Guba, E. F. Injury to greenhouse plants from hydrocyanic acid gas, following the application of copper fungicides. Phytopath. 16:633-634. 1926.
4. ———, Incompatibility of copper fungicides and hydrocyanic acid gas in the greenhouse. Amer. Produce Grower 1:12. 1926.
5. Hodgman, C. D., and Lange, N. A. Handbook of chemistry and physics. 10th ed. Chemical Rubber Publishing Co., Cleveland, Ohio. 1922.
6. Holland, E. B., Dunbar, C. O., and Gilligan, G. M. The preparation and effectiveness of basic copper sulfates for fungicidal purposes. Jour. Agr. Research 33:741-751. 1926.
7. ———, Dunbar, C. O., and Gilligan, G. M. Influence of form and proportion of lime used and of method of mixing on the resulting Bordeaux mixture. Jour. Agr. Research 34:677-686. 1927.
8. ———, Dunbar, C. O., and Gilligan, G. M. Supplements for copper fungicides. Mass. Agr. Expt. Sta. Bul. 252. 1929..
9. ———, Dunbar, C. O., Gilligan, G. M., and Doran, W. L. The preparation and effectiveness of basic copper sulfate as a fungicide. Mass. Agr. Expt. Sta. Bul. 254. 1929.
10. ———, and Gilligan, G. M. Chemical hydrated lime for the preparation of Bordeaux mixture. Phytopath. 17: 571-572. 1927.
11. ———, and Gilligan, G. M. Classification of copper fungicides. Phytopath. 18:455-458. 1928.
12. Pickering, S. U. Copper salts and their behavior with alkalis. Jour. Chem. Soc. (London) 101 (Pt. 1) :174-192. 1912.
13. Quayle, H. J. Bordeaux spraying and fumigation injury. Calif. Citrogr. 18 (No. 6): 166, 184. 1933.
14. Ridgway R. Color standards and color nomenclature. Washington, D. C. 1912.
15. Williams, H. E. The chemistry of cyanogen compounds. 423 pp. A. Churchill, London. 1915. (Lit. cited pp. 48-51.)

PUBLICATION OF THIS DOCUMENT APPROVED BY COMMISSION ON ADMINISTRATION AND FINANCE
3M-1-'34. No. 268.